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HISTORY OF COATED PARTICLES*

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The history of coated-particle fuels can be traced to the period, 1945 to 1947, when work began on the Daniels' Pile at the Clinton Laboratories, later Oak Ridge National Laboratory (ORNL). The proposed fuel consisted of a dispersion of UO_2 particles in a graphite matrix. Fabrication methods included calcining of graphite impregnated with uranyl nitrate or extruding a mixture of graphite, UO_2, and binder. Early irradiation results of R. H. Kernohan showed that the proposed fuel suffered from severe fission-gas release and also rapid shrinkage due to recoil damage.[1] The need for larger particle sizes to reduce recoil damage initiated interest in fuel microspheres.

Although work on the Daniels' Pile was discontinued in 1947, the development of cermet and ceramic-based dispersion fuels continued at ORNL under the direction of J. R. Johnson, later with the 3M Company, and J. M. Warde during the period, 1951–56 in support of the Aircraft Nuclear Propulsion (ANP) Program. Similar work was also under way at Battelle Memorial Institute (BMI) throughout the 1950s. The BMI group — consisting of A. K. Smalley, R. C. Riley, W. H. Duckworth, J. M. Blocher, and J. H. Oxley — was studying fluidized-bed vapor-deposition processes for making both metal- and ceramic-coated oxides. Since the air coolant was exhausted to the atmosphere, fission-produce release was a serious concern. Coatings on either the fuel particles or fuel elements were

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proposed to prevent the release. Inasmuch as the fuel had to be compatible with air at high temperatures, the experimental matrices and coatings were oxides except for one type, consisting of siliconized SiC over graphite.

In 1956, Sanderson and Porter Company (S & P) initiated a study of a high-temperature, all-ceramic, helium-cooled reactor. After considering emitting versus fission-product retentive fuels, the S & P fuels team – consisting of S. T. Robinson, R. Benenati, and L. D. Stoughton – opted for retentive fuels using either particle or element coatings. Robinson and Benenati had consulted with 3M and were familiar with J. R. Johnson's work. Sanderson and Porter sought to develop commercial sources for coated particles or elements, including 3M, BMI, National Carbon Company* (NC), High-Temperature Materials (HTM), and American Metal Products. Irradiation tests conducted at BMI and ORNL showed that coatings on elements failed quickly, but a test conducted in 1960 by BMI on a S & P fuel element containing UO_2 microspheres with Al_2O_3 coatings was decisive in pointing toward the coated-particle approach.[2] Compatibility problems between Al_2O_3 and graphite caused most people to opt for pyrolytic-carbon (PyC) coatings on carbide kernels.

Independently of the U. S. effort, a small team was formed at the Atomic Energy Research Establishment (AERE), Harwell, early in 1956, to investigate the High-Temperature Gas-Cooled Reactor (HTGR) System. John Sayers, R. A. U. Huddle, and Peter Murray participated in the fuel-development aspects. After three years of study, the United Kingdom Atomic Energy Authority (UKAEA) transferred the program to the

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international Organization of European Economic Cooperation (OEEC); and the Dragon Project was born. Some work was done at Harwell on coated particles, but emitting fuels were favored in the reference design.

Also, in the late 1950s, General Atomic (GA) decided to pursue the HTGR. W. V. Goeddel and D. H. Durinsky, visiting scientist from Brookhaven National Laboratory, were in charge of the fuel-development program. Early in the program, the GA team had serious problems with the hydrolysis of mixed $(Th,U)C_2$. Goeddel and Gurinsky proposed PyC coatings on the carbide kernels to prevent the reaction. They obtained their first coated particles from BMI in October 1959. Though GA decided to use coated particles for fabrication reasons, both the Dragon and GA reference designs consisted of purged emitting fuels in impermeable-graphite sleeves. Consequently, initial GA coatings were expected to fail early during irradiation. When it turned out to be difficult and expensive to fabricate the low-permeability graphite, the approaches of Dragon and GA also turned to coated particles for fission-product retention.

In 1960, ORNL began a program in support of the S & P Pebble-Bed Reactor to test coated particles supplied by various commercial firms, including 3M, NC, and HTM. W. D. Manly directed the materials' aspects of the program, and O. Sisman and D. B. Trauger were responsible for irradiation testing. Early irradiation results showed that monolayer coatings were poor, presumably because of fission-recoil damage. One supplier, National Carbon, experienced with reactor-grade graphites, decided to pursue high-temperature, isotropic PyC because of its superior radiation stability; but coating failures occurred during fabrication that were attributed to differential thermal expansion between the carbide kernel and the coating. Therefore, R. A. Reuter and R. L. Finicle developed a two-layer coating with a low-density inner

layer and a high-density outer coating. This duplex design was found to have outstanding irradiation behavior, and modifications of it became the universal reference.

During the late 1950s, Brown, Boveri, Krupp (BBK) in Germany decided to build a pebble-bed reactor (AVR) at Jülich. Fuel development was the responsibility of B. Liebmann of NUKEM. When efforts to seal the graphite sphere failed, BBK purchased fuel elements containing particles with duplex coatings from NC. W. P. Eatherly was in charge of the NC fuel program. The performance of the NC elements exceeded design burn-up limitations; and, in fact, many of the elements are still being irradiated.

Spurred by good irradiation results, vigorous programs of fuel fabrication, characterization, and recycle development were pursued by several laboratories around the world. J. C. Bokros at GA and R. L. Beatty, F. L. Carlsen, Jr., and J. L. Cook of ORNL found that a wide variety of coatings could be fabricated, depending upon coating temperature, coating gas, and supply rate and that the key coating attributes were geometry, density, and isotropy.[3,4] Bokros and R. J. Price at GA conducted a series of irradiations on PyC strips and particles that showed the importance of fast-neutron irradiation on the behavior of PyC coatings.[5] Based on their work and knowledge of the duplex-particle results, J. W. Prados and J. L. Scott developed a theoretical model to describe two-layer coating behavior.[6,7]

In 1965, R. L. Beatty began a master's thesis on the use of propane as a coating gas. This work eventually led to the development of low-temperature isotropic (LTI) coatings.[8] Propylene was found to be preferable to propane, because its decomposition is less endothermic.

In the early years, most workers concentrated on UC_2 or $(U,Th)C_2$ as fuel kernels. However, workers at ORNL interested in fuel recycle,

and especially remote fuel fabrication, were particularly concerned about the hazards of handling pyrophoric carbides. D. E. Ferguson, O. C. Dean, and D. A. Douglas, Jr. proposed sol-gel-derived oxide fuels instead.[9] Subsequent heat treatments and irradiation tests showed that compatibility between the oxide kernels and PyC coatings was no problem as long as the coatings remained intact.

Attention then turned to the problem of solid fission-product release. By 1961, several investigators had noted that barium, cesium, and strontium diffused through intact-PyC coatings. In 1966, John Sayers, E. Gleuckauf, and John de Nordwall at Harwell demonstrated the ability of SiC coatings to prevent this release.[10] The Dragon Project conducted much development on coatings containing SiC barrier layers and adopted the design for the first charge fuel for the Dragon Reactor. Subsequently, GA developed the Triso-particle design for use with Fort St. Vrain and large HTGR fuel; and J. L. Kaae developed a computer code describing its behavior.[11]

The next major problem associated with coated particles was found during prototypic fuel-element irradiations. The kernels migrated through the coating up the temperature gradient. This phenomenon, called the amoeba effect, occurs with both oxides and carbides. Careful work at a number of sites has led to temperature design limits which preclude amoeba failures.

Now, indications are that fuel elements containing coated particles can be built with a high degree of reliability with a low probability of fission-product release. Future developments will be directed at lower fabrication costs, better resistance to amoeba migration, and techniques for fuel recycle.

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